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TI Supported catalysts containing platinum-group metal for preparation of diaryl carbonates

IN Buysch, Hans-Josef; Hesse, Carsten; Jentsch, Joerg-Dietrich; Rechner, Johann; Zirngiebl, Eberhard

PA Bayer A.-G., Germany

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AB Supported catalysts contg. a Pt-group metal such as Pd or Rh and another metal such as Mn, Co, Cu, or V show high activity and selectivity during the prepn. of diaryl carbonates [e.g., $(PhO)_2CO$] from an arom. OH compd., CO, and O in the presence of a quaternary salt and a base.

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PLATINUM METAL-CONTAINING SUPPORTED CATALYSTS AND METHOD FOR THE PREPARATION OF DIARYLCARBONATES

Inventors:

Dr. Hans-Josef Buysch
47809 Krefeld (DE)

Dr. Carsten Hesse
47800 Krefeld (DE)

Dr. Jörg-Dietrich Jentsch
45468 Mühlheim (DE)

Dr. Johann Rechner
47906 Kempen (DE)

Dr. Eberhard Zirngiebl
51061 Cologne (DE)

Applicant:

BAYER AG
51368 Leverkusen (DE)

[Abstract]

In the method for the preparation of an aromatic carbonate from an aromatic hydroxy compound, CO and O_2 in the presence of quaternary salt and a base using a platinum metal catalyst and a cocatalyst, it is advantageous to use supported catalysts, which contain, in the reactive state (i) a platinum metal, a platinum metal halide, or a platinum metal halide complex compound, and (ii) a cocatalytically acting metal compound from the groups IB, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, the iron group (atomic numbers 26-28) or the rare earth metals (atomic numbers 58-71) of the periodic table of elements (Mendelyeer), always in a quantity of 0.01-15 wt%, calculated as metal and with respect to the total weight of the catalyst.

Description

The present invention concerns platinum metal-containing supported catalysts and their use in methods for the manufacture of diarylcarbonates by the reaction of aromatic hydroxy compounds with carbon monoxide and oxygen, which are characterized by the fact that the supported catalysts contain, in addition to the platinum metal, at least one cocatalyst.

It is known how to manufacture organic carbonates by the oxidative reaction of aromatic hydroxy compounds with carbon monoxide in the presence of a noble metal catalyst (DE-OS 2,815,512). It is preferred to use palladium as the noble metal. In addition, a cocatalyst (for example, manganese or cobalt salts), a base, a quaternary salt, various quinones or hydroquinones and desiccants can be used. In this context, it is possible to work in a solvent, preferably methylene chloride.

Activity and selectivity are not the only factors important in the scientific implementation of this process, the effective recovery of the noble metal catalyst is of crucial importance: On the one hand, the noble metal catalyst represents a considerable cost factor. Losses of noble metal catalyst must be replaced at considerable cost. On the other hand, no residues of the noble metal catalyst must remain in the product. So far, the economic and effective recovery of homogeneous catalysts has not been described for the process of oxidative carbonylation of aromatic hydroxy compounds to form diarylcarbonates. The separation of a noble metal catalyst from a liquid reaction mixture, for example, by filtration or centrifugation, can occur at a low cost if, for example, heterogeneous support catalysts are used.

For the preparation of supported catalysts, suitable materials are known. Depending on the type of the process, supports with large internal surface area, such as, for example, aluminum oxide, magnesium oxide, activated carbon or silicon dioxide having a surface area of more than 50 m^2 per gram, supports with surface areas of approximately 5 m^2/g and correspondingly larger

pore radii, such as, for example, rust, titanium dioxide, iron oxide or zinc oxide or coarse particle supports, such as silicon carbide and corundum (Ullmanns Enzyklopädie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], 3rd edition, Berlin/Munich, 1957, Volume 9, pp. 263 ff.). In principle, it is possible to use either synthetic materials, such as activated aluminum oxides, silica gels, silicates, titanium dioxides or activated carbons, or materials made of natural sources, such as, for example, pumice, kaolin, bleaching earth, bauxite, bentonite, kieselguhr, asbestos or zeolites. In EP 572,980, EP 503,581 and EP 614,876, noble metal supported catalysts are used, which contain 5% Pd on carbon supports. Nevertheless, such supported catalysts, according to our own examinations, produce very unsatisfactory results, and no conversions, so that, for such an economic process control, they too are not suited for an economic process control. In Japanese Patent No. JP 01/165,551 (cited according to C.A. 112 (1990), 76618j) a description is provided for the manufacture of aromatic palladium carbonates or Pd compounds, such as Pd acetylacetonate, in combination with (earth)alkali iodides or onium iodides, such as tetrabutylammonium iodide, and at least one zeolite. In JP 04/257,546 and JP 04/261,142, one example is provided for each of the supported catalysts in the manufacture of aromatic carbonates, in which silicon carbide granulate is used as support material for supported catalyst in a distillation column. Although, in the examples in question, the operating conditions used are stringent (high pressure, high temperature), this catalyst allows only very low time-space yields. These low time-space yields make the manufacture of aromatic carbonates with such supported catalysts the economically impossible.

Thus, so far no supported catalyst is available, by means of which diarylcarbonates can be manufactured economically by the conversion of an aromatic hydroxy compound with carbon oxide and oxygen. Therefore, the task was to find a supported catalyst with high activity and selectivity, which allows the economically efficient manufacture of diarylcarbonates by the conversion of an aromatic hydroxy compound with carbon monoxide and oxygen.

It has now been found that the represented drawbacks can be overcome if platinum metal supported catalysts are used which contain, in addition to the platinum metal, also at least one cocatalyst. The catalysts made of platinum metal and at least one cocatalyst on a support are used according to the invention as powders, tablets and binder-containing extrudate. Suitable binders are, for example, SiO_2, Al_2O_3 or clay minerals. The binder contents can be varied in a broad range, for example, 0.5-99.5 wt%, with respect to the total weight of the support.

The supported catalysts according to the invention contain, in the reactive state, (i) a platinum metal, platinum metal halide or a platinum metal halide-containing complex compound or a compound which can be transferred under the conditions of the reaction into a platinum metal, platinum metal halide or a platinum metal halide-containing complex compound, in a quantity of 0.01-15 wt%, preferably 0.05-10 wt%, calculated as platinum metal and with respect

to the total weight of the catalyst, and (ii) a cocatalytically acting metal compound from the groups IB, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, the iron group (atomic numbers 26-28) or the rare earth metals (atomic numbers 58-71) of the periodic table of elements (Mendelyeer) in a quantity of 0.01-15 wt%, preferably 0.05-10 wt%, calculated as metal, and with respect to the total weight of the catalyst.

Such catalysts are available as heterogeneous catalytic systems, and thus they facilitate the separation of the reaction product from expensive platinum metal, compounds thereof and the cocatalyst.

The invention relates to a method for the manufacture of an aromatic carbonate having the formula

$$R\text{-}O\text{-}CO\text{-}O\text{-}R \qquad \text{(I)}$$

in which

R denotes substituted or unsubstituted C_6-C_{12} aryl, preferably substituted or unsubstituted phenyl, and, in particular, unsubstituted phenyl is especially preferred,

by reacting an aromatic hydroxy compound having the formula

$$R\text{-}O\text{-}H \qquad \text{(II)}$$

in which R has the above indicated meaning,

with carbon monoxide and oxygen in the presence of quaternary ammonium or phosphonium salt and a base at 30-200EC, preferably 30-150EC, in particular 40-120EC, and at a pressure of 1-150 bar, preferably 2-50 bar, and in particular 5-25 bar, characterized in that platinum metal supported catalysts are used which, in addition to the platinum metal, contain one or more cocatalysts of the above-described type and in the above-described quantity.

As an example of the formation of diphenylcarbonate, the method according to the invention can be represented by the following equation:

//insert, equation p.3//

For the use according to the invention as catalyst support, all industrially conventional catalyst supports are suitable, for example, those made on the basis of coal, elemental oxides, elemental carbides, and elemental salts in various application forms. Examples of such carbon containing supports are coke, graphite, rust and activated carbon. Examples of elemental oxide catalyst supports are SiO_2 (natural or synthetic salicylic acids, quartz), Al_2O_3 (α-, γ-Al_2O_3), clay

earths, natural and synthetic alumosilicates (zeolites), TiO_2 (rutile, anatase), ZrO_2 and ZnO. Examples of elemental carbides and salts are SiC, $AlPO_4$, $BaSO_4$, $CaCO_3$, etc. They can be used both in the sense of chemically uniform pure substances and in a mixture. For the use according to the invention as catalyst supports, materials in the form of pieces or powder are both suitable. For the case of the arrangement of the supported catalyst as a solid bed, the support is preferably used in the form of a shaped substance, for example, as beads, cylinders, rods, hollow cylinders, rings, etc. If desired, catalyst supports can be further modified by extrusion, tablet formulation, optionally with the admixture of additional catalyst supports or binders such as SiO_2 or Al_2O_3, and by calcining. The preparation and the processing of the catalyst supports used according to the invention are well known to the person skilled in the art and in the prior art.

The reactive component of the catalysts consists, in the reactive state, of a platinum metal, a platinum metal halide, such as $PdCl_2$ or $PdBr_2$, or a platinum metal halide-containing complex compound, which additionally can contain, for example, olefins, amines, phosphines, nitrile, carbon monoxide or water, such as $A_2(PdHal_4)$, where A denotes, for example, Li, Na, K, NH_4, Rb, Cs, NR^1_4, with R^1: organic residue C_6-C_{10} aryl, C_7-C_{12} aralkyl and/or C_1-C_{20} alkyl residue, and Hal denotes halogen, such as, for example, F, Cl, Br, I, and at least one cocatalyst. Suitable platinum metal complex compounds are fundamentally known. Examples are: $Li_2(PdCl_4)$, $Na_2(PdCl_4)$, $K_2(PdCl_4)$, $(NBu_4)_2(PdCl_4)$, $Na_2(PdBr_4)$, $K_2(PdBr_4)$, $(NBu_4)_2(PdBr_2)$ (where Bu = n-butyl). Examples of olefin-containing platinum metal complexes are [allylpalladium chloride] dimer -$[C_3H_5PdCl]_2$, 1,5-cyclooctadienpalladium chloride-$C_8H_5PdCl_2$. Examples for phosphine-containing platinum metal complexes are [1,2-bis(diphenylphosphino)ethane]palladium dichloride +$Pd[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Cl_2$, bis(triphenylphosphino)palladium dichloride +$Pd[P(C_6H_5)_3]_2Cl_2$. Examples of amine-containing platinum metal complexes are diaminopalladium dibromide +$Pd(NH_3)_2Br_2$ diaminopalladium dichloride-$Pd(NH_3)_2Cl_2$, tetraaminopalladium tetrachloropalladate +$[Pd(NH_3)_4][PdCl_4]$, examples for nitrile-containing platinum metal complexes are bis(acetonitrile)palladium dichloride +$Pd(CH_3CN)_2Cl_2$, bis(benzonitrile)palladium dichloride, -$Pd(C_6H_5CN)_2Cl_2$, examples of carbon monoxide-containing platinum metal complexes are tetrabutylammonium tribromocarbonylpalladate +$(NBu_4)Pd(CO)Br_3$ (where Bu = n-butyl) and tetrabutylammonium trichlorocarbonyl palladate +$(NBu_4)Pd(CO)Cl_3$ (where Bu = n-butyl). In the mentioned examples, Pd was mentioned as a platinum metal, but other platinum metals can also be considered, such as Pt, Ir, Ru or Rh; Pd and Rh are however preferred, particularly Pd. The platinum metal has a valency range from 0 to 4.

Furthermore, it has been shown that the platinum metal halide, or the platinum metal halide-containing complex compound, can be manufactured in situ during the preparation or during the catalyst use under reaction conditions from a suitable halide-free platinum metal

compound and a halide-containing compound on the support. As halide-free platinum metal compounds it is possible to use, for example, platinum metal nitrates, -acetates, -propionates, -butyrates, -oxalates, -carbonates, -oxides, -hydroxides, -acetylacetonates and other compounds with which a person skilled in the art is familiar. As halide-containing compounds it is possible to consider halide-containing salts or complex compounds of the first elements of the fifth main group and of the first to eighth secondary group of the periodic table of elements (Mendelyeer) and the rare earth metals (atomic number 58-71) or aliphatic halogenated hydrocarbons. Examples are NaBr, NaCl, $MgCl_2$, $MgBr_2$, $AlCl_3$, CH_2Cl_2, $NaPF_6$, $MnCl_2$, $MnBr_2$, $CoBr_2$, $CeCl_3$, SmI_2, $CuCl_2$, Na_2ZnCl_4, $TiCl_4$ and NR^1_4Br, where R^1 has the above mentioned meaning.

The quantity of the platinum metal, platinum metal halide or platinum metal halide-containing complex compound, in the reactive state, is 0.01-15 wt%, preferably 0.05-10 wt%, calculated as platinum metal, and with respect to the total weight of the catalyst.

As cocatalyst for the method according to the invention, it is possible to use a metal compound of the groups IB, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, the iron group (atomic numbers 26-28) or the rare earth metals (atomic numbers 58-71) of the periodic table of elements (Mendelyeer), preferably Mn, Cu, Co, V, Nb, W, Zn, Ce and Mo, preferably Mn, Co, Cu, Mo and Ce. The metals can be used as halides, oxides, carboxylates of C_2-C_6 carboxylic acids, diketonates or nitrates, and as complex compounds which can contain, for example, carbon monoxide, olefins, amines, nitriles, phosphines and halides.

The quantity of the cocatalyst containing compound in the reactive state is 0.01-15 wt%, preferably 0.05-10 wt%, calculated as metal and with respect to the total weight of the catalyst.

Platinum metal and cocatalyst can be applied simultaneously, that is from a shared solution, or subsequently in any sequence on the support. Suitable solvents for the platinum metal and cocatalyst compounds for the manufacture of supported catalysts according to the invention are, for example, water, aliphatic hydrocarbons, such as pentane, n-hexane, cyclohexane, etc., aliphatic halogenated hydrocarbons, such as dichloromethane, trichloromethane, etc., unsaturated hydrocarbons, such as pentene, isoprene, cyclopentadiene, hexenes, hexines, cyclohexenes, cyclooctadienes, etc., aromatic hydrocarbons, such as benzene, toluene, xylene, etc., halogenated aromatic hydrocarbons, such as chlorobenzene, dichlorobenzene, etc., primary, secondary or tertiary alcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, cumyl alcohol, iso-amyl alcohol, diethylene glycol, etc., ketones, such as acetone, 2-butanone, methyl isobutyl ketone, acetylacetone, etc., ethers, such as diethyl ether, diisopropyl ether, methyl t-butyl ether, dioxane, tetrahydrofuran, etc., esters such as methyl acetate, ethyl acetate, etc., nitriles, such as acetonitrile, benzonitrile, etc., carbonates, such as dimethyl carbonate, diethyl carbonate,

diphenyl carbonate, etc., amides, such as dimethylacetamide, N-methylpyrrolidinone and tetramethyl urea. Naturally it is also possible to use mixtures of such solvents.

The manufacture of the catalysts, according to the invention, is carried out according to the methods which are fundamentally known to a person skilled in the art. Thus it is possible to apply onto the catalyst support to be used, according to the invention, solutions of one or more of the mentioned platinum metal compounds and of the mentioned halide-containing compounds, as well as one or more cocatalysts, for example, by soaking, adsorption, immersion, spraying, impregnation and ion exchange. Furthermore, it is possible to fix one or more platinum metals, the mentioned halide-containing compounds, as well as one or more cocatalysts by precipitation with a base onto the support. It is possible to use a base, for example, (earth)alkali metal hydroxides, such as $Ca(OH)_2$, $Mg(OH)_2$, NaOH, LiOH and KOH, (earth)alkali metal hydrogen carbonates, such as $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $NaHCO_3$, $LiHCO_3$ and $KHCO_3$, (earth)alkali metal carbonates such as $CaCO_3$, $MgCO_3$, Na_2CO_3, Li_2CO_3 and K_2CO_3, alkali metal salts of weak organic acids, such as sodium acetate, potassium acetate and lithium acetate, and (earth)alkali metal salts of substituted and unsubstituted phenols (the substituted phenols are those described below as usable in the method for the manufacture of diaryl carbonate), such as lithium phenolate, sodium phenolate, sodium cresolate and calcium phenolate. The platinum metal and the halide-containing compound can be applied in any order, successively or simultaneously, onto the support. A variant of the invention comprises the application of the platinum metal by precipitation of a platinum metal halide or a platinum metal halide complex compound with a suitable base (possibilities include, for example, those described above), reduction of the precipitated platinum metal base to metal with an appropriate reducing agent, such as, for example, hydrazine, formaldehyde, Na formiate, $NaBH_4$ at temperatures of 0-200EC, or gaseous hydrogen at temperatures of 0-500EC, preferably 20-300EC, in particular 30-250EC, and the reaction of the platinum metal with hydrogen halide or gaseous halogen at temperatures of 20-600EC, preferably 50-500EC.

During the application of platinum metal and cocatalysts onto the support, the mixture can be stirred. However, it can also be advantageous to allow the mixture to stand, or to shake it, so that any shaped substances that may have been optionally used are not damaged by a stirrer. After the application of platinum metal and cocatalyst onto the support, the supported catalyst is separated, for example, by filtration, sedimentation or centrifugation. In an additional variant of the invention, the solvent is separated by distillation.

After distillation of the solvent, the supported catalysts so obtained are dried. This can be carried out in the air, in a vacuum or in a gas flow. Suitable gases for the drying of the supported catalyst in the gas flow are nitrogen, oxygen, carbon monoxide, carbon dioxide or rare gases, as well as any mixtures of the mentioned gases, preferably, for example, air. Gaseous hydrocarbons

are also suitable, such as alkanes (for example, methane, ethane, propane), alkenes, such as ethene, propene, butene, butadiene and alkynes, such as ethyne, propyne, etc., in any composition. The drying is carried out at 20-200EC, preferably 40-180EC, in particular 60-150EC. The drying time depends, for example, on the porosity of the support used and on the solvent used. In general it is several hours, for example, 0.5-50 h, preferably 1-40 h, in particular 1-30 h.

After the drying, the dried supported catalysts can be calcined. This is carried out in air, in a vacuum or in the gas flow. Suitable gases for the calcining of the supported catalyst in the gas flow are, for example, nitrogen, oxygen, carbon dioxide or rare gases, as well as any mixtures of the mentioned gases, preferably, for example, air. The calcining occurs at 100-800EC, preferably 100-700EC, particularly preferable 100-600EC. In this context, it can possibly be advantageous if, during the calcining, the composition of the gas is changed abruptly or continuously. An abrupt change in the composition of the calcining gas can occur, for example, by increasing the O_2 content after 10 h from 10 to 20 vol% and maintaining it at that level for the remaining 10 h, while maintaining the same the temperature. A continuous change in the composition of the calcining gas can occur, for example, by increasing, while maintaining the temperature the same, within 20 h the oxygen content from 0 to 20 vol% at 1 vol% increase/h. The calcining time in general is several hours, for example, 0.5-50 h, preferably 1-40 h, particularly 1-30 h.

The aromatic hydroxy compounds that can be reacted with the supported catalysts according to the invention are, for example, phenol, o-, m- or p-cresol, o-, m- or p-chlorophenol, o-, m- or p-ethylphenol, o-, m- or p-propylphenol, o-, m- or p-methoxyphenol, 2,6-dimethylphenol, 2,4-dimethylphenol, 3,4-dimethylphenol, 1-naphthol, 2-naphthol and bisphenol A, preferably phenol. In general, in the case of a substitution of the aromatic hydroxy compound with 1 or 2 substituents, the substituents are C_1-C_4 alkyl, C_1-C_4 alkoxy, fluorine, chlorine or bromine.

For the method according to the invention, it is possible to use any organic or inorganic, bases or mixtures thereof. Examples of inorganic bases are, without limiting the method according to the invention, alkali metal hydroxides and carbonates, carboxylates or other salts of weak acids as well as alkali salts of aromatic hydroxy compounds having the formula (II), for example, alkali metal phenolates. Naturally, in the method according to the invention, it is also possible to use the hydrates of alkali metal phenolates. Examples of such a hydrate mentioned here, without limiting the method according to the invention, comprise the sodium phenolate trihydrate. The quantity of admixed water is, however, preferably measured in such a manner that a per mol base maximum of 5 mol of water is used. The consequences of using higher water concentrations include worse yields and the decomposition of formed carbonates. Organic bases mentioned, without limiting the method according to the invention, include tertiary amines,

which can carry as organic residues C_6-C_{10} aryl, C_7-C_{12} aralkyl and/or C_1-C_{20} alkyl residues, or pyridine bases or hydrated pyridine bases, for example, triethylamine, tripropylamine, tributylamine, trioctylamine, benzyldimethylamine, dioctylbenzylamine, dimethylphenethylamine, 1-dimethylamino-2-phenylpropane, pyridine, N-methylpiperidine, and 1,2,2,6,6-pentamethylpiperidine. It is preferred to use as base an alkali salt of an aromatic hydroxy compound; it is particularly preferred to use an alkali salt of the aromatic hydroxy compound (II), which is also to be reacted to form the organic carbonate. These alkali salts can be lithium, sodium, potassium, rubidium or cesium salts. It is particularly preferable to use lithium, sodium and potassium phenolate, in particular sodium phenolate.

The base can be added to the reaction mixture as a pure compound in solid form or as a smelt. In an additional variant of the invention, the base is added to the reaction mixture as a solution which contains 0.1-80 wt%, preferably 0.5-65 wt%, in particular 1-50 wt%, of the base. In this context, both alcohols or phenols can be used as solvent, for example, the phenol to be reacted (II), as well as inert solvents. The inert solvents mentioned are those listed below under reaction media.

These solvents can be used alone or in any combination. Thus, a variant of the method according to the invention consists, for example, of dissolving the base in a phenol melt, which is diluted with a solvent. It is preferred to dissolve the base in a melt of an aromatic hydroxy compound, and in particular in a smelt of the aromatic compound (II), which is to be converted to the organic carbonate. It is particularly preferred to add the base dissolved in phenol. The base is added in a quantity which is independent of the stoichiometry. The ratio of platinum metal, for example, palladium, to base is preferably chosen in such a manner that, per mol of platinum metal, for example, palladium, 0.1-500, preferably 0.3-200, and particularly preferable 0.9-130 equivalents of base are used.

The method according to the invention is preferably carried out without solvent. Naturally, it is also possible to use inert solvents. Examples of solvents mentioned include dimethylacetamide, N-methylpyrrolidinone, dioxane, t-butanol, cumyl alcohol, isoamyl alcohol, tetramethyl urea, diethylene glycol, halogenated hydrocarbons (for example, chlorobenzene or dichlorobenzene) and ether.

The quaternary salts used in the context of the present invention can be, for example, organic residues of substituted ammonium or phosphonium salts. Suitable for the method according to the invention are ammonium and phosphonium salts, which carry as organic residues C_6-C_{10} aryl, C_7-C_{12} aralkyl and/or C_1-C_{20} alkyl residues, and as an anion halide, tetrafluoroborate or hexafluorophosphate. It is preferred to use, in the method according to the invention, ammonium salts which carry as organic residues C_6-C_{10} aryl, C_7-C_{12} aralkyl and/or C_1-C_{20} alkyl residues and an anion halide, tetrabutylammonium bromide is particularly preferred.

The quantity of such a quaternary salt is 0.1-50 wt%, with respect to the weight of the reaction mixture. It is preferred for this quantity to be 0.5-15 wt%, in particular 1-5 wt%.

The method according to the invention is preferably carried out without solvent, at 30-200EC, preferably 30-150EC, particularly 40-120EC, and at a pressure of 1-150 bar, preferably 2-50 bar, particularly 5-25 bar.

The supported catalysts can be used as powders or shaped substances, and they can again be separated from the reaction mixture, for example, by filtration, sedimentation or centrifugation.

The manufacture of aromatic carbonates with the supported catalysts according to the invention can be carried out in various variants. A first possibility consists in the batch mode. In the case of a continuous mode in countercurrent or cocurrent, or in the silica phase on the solid bed catalyst, loads of 0.01-20 g of aromatic hydroxy compound per gram of supported catalyst per hour, preferably 0.05-10 g of aromatic hydroxy compound per gram supported catalyst per hour, per in particular 0.1-5 g of aromatic hydroxy compound per gram of supported catalyst per hour are regulated. The supported catalysts used in the batch tests can be repeatedly used without cleaning if the same process substances are used. In the continuous mode, the supported catalysts used can remain in the reactor for a long time. It is preferred to use a continuous mode of operation in an individual reactor in the case of the use of the supported catalysts according to the invention, or in a cascade of reactors.

If the supported catalyst is used as powder, then, for the mixing of the reaction components, the stirred containers used are equipped with appropriate stirrers. If the supported catalyst powders are used as a suspension in stirred vessels or bubble columns, quantities of 0.001-50 wt%, preferably 0.01-20 wt%, and in particular 0.1-10 wt%, of supported catalyst powder, with respect to the quantity of aromatic hydroxy compound used, are used. In particularly preferred variants, the heterogeneous supported catalyst is used as shaped substance, in a fixed position in stirred vessels, bubble columns, trickle-bed phase reactors or cascades of these reactors, where the different reactor types can also occur simultaneously in a cascade.

Examples

Example 1

a) Application of palladium and manganese on a powdered titanium dioxide:

To a slurry of 283.5 g of titanium dioxide powder (manufacturer Norton) in 1500 mL of water, 300 mL of a solution of 40.5 g (0.16 mol) of manganese(II)-nitrate-4-hydrate in water are added at room temperature. An adjustment to alkalinity is then made with diluted soda lye. The

resulting suspension is removed by suction, washed with water, dried at 100EC, and annealed for 3 h at 300EC. The support doped with manganese was prepared in a slurry with 1500 mL of water and reacted with 300 mL of a solution containing 50 g of sodium tetrachloropalladate(II) solution with 15% palladium. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension obtained was removed by suction, washed, and dried at 100EC. The catalyst contained 2.5 wt% of Pd and 3 wt% of Mn, each calculated as metal.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

In an autoclave (1-L) with an aeration stirrer, cooler and downstream cold trap, 8.31 g of tetrabutylammonium bromide were dissolved in 450 g of phenol at 80EC. Then 4 g of the above-described supported catalyst and 2.21 g of sodium phenolate, dissolved in 50 g of phenol, were used. While introducing a gas mixture consisting of carbon monoxide and oxygen (95:5 volume%), the pressure was adjusted to 10 bar. The quantity of the gas mixture was adjusted at 300 NL/h. Every hour, a sample from the reaction mixture was removed and analyzed by gas chromatography. The analyses showed that, after 1 h, 8.1% of diphenylcarbonate, after 2 h, 14.3% of diphenylcarbonate; and after 3 h, 18.6% of diphenylcarbonate were contained in the reaction mixture. 14.1 g of a phenol/water mixture were condensed in the cold trap.

c) An additional catalyst sample of Example 1a) was used under the same reaction conditions, except that

in addition, a homogeneously dissolved cocatalyst, namely 0.77 g of manganese acetyl acetonate, was present. Every hour a sample of the reaction mixture was collected and analyzed by gas chromatography. The analyses showed that: after 1 h, 8.3% of diphenylcarbonate; after 2 h, 14.5% of diphenylcarbonate; and after 3 h, 18.5% of diphenylcarbonate were contained in the reaction mixture. 13.9 g of a phenol/water mixture were condensed in the cold trap. The presence of a homogeneously dissolved cocatalyst does not produce a better result, and it is thus no longer necessary according to the invention.

Example 2

a) Application of palladium and cobalt to a powdered titanium dioxide:

To a slurry of 18.75 g of palladium(II) bromide (0.07 mol), 28.5 g of sodium bromide (0.28 mol) and 33.4 g of cobalt(II) bromide (0.15 mol) in 1500 mL of water, 283.5 g of titanium dioxide powder (Norton) were added at room temperature. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension was removed by suction, washed and dried at 100EC. The catalyst contained 2.5 wt% of Pd and 3 wt% of Co, each calculated as metal.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 6.1% of diphenylcarbonate; after 2 h, 11.3% of diphenylcarbonate; and after 3 h, 15% of diphenylcarbonate were contained in the reaction mixture. 11.5 g of a phenol/water mixture were condensed in the cold trap.

Example 3

a) Application of palladium and manganese to a titanium dioxide extrudate:

200 mL of titanium dioxide extrudate were soaked with 58.4 mL of a solution of 21.6 g of manganese(II) chloride in water. A drying step was then carried out under nitrogen at 110EC. The support doped with manganese was then soaked with 58 mL of an aqueous solution containing 33.3 g of sodium tetrachloropalladate(II) solution with 15% palladium. A drying step was then carried out under nitrogen at 110EC. The finished contact catalyst contained, per liter, 25 g of Pd and 30 g of Mn, each calculated as metal.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1, except that the catalyst was fixed in a mesh wire basket. The analyses showed that: after 1 h, 4.6% of diphenylcarbonate; after 2 h, 8.7% of diphenylcarbonate; and after 3 h, 11.6% of diphenylcarbonate were contained in the reaction mixture. 9.2 g of a phenol/water mixture were condensed in the cold trap.

Example 4

a) Application of rhodium and manganese to a titanium dioxide extrudate:

200 mL of titanium dioxide extrudate were soaked with 58.4 mL of a solution of 21.6 g of manganese(II) chloride in water. Then, a drying step was carried out under nitrogen at 110EC. The support doped with manganese was then soaked with 58 mL of aqueous solution, containing 12.94 g of rhodium(III) hydrochloride. A drying step was then carried out under nitrogen at 110EC. The contact catalyst contained, per liter, 25 g of rhodium and 30 g of Mn, each calculated as a metal.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 3. The analyses showed that: after 1 h, 1.4% of diphenylcarbonate; after 2 h, 2.9% of diphenylcarbonate; and after 3 h, 4.1% of diphenylcarbonate were contained in the reaction mixture. 3.5 g of a phenol/water mixture were condensed in the cold trap.

Example 5

a) Application of palladium and manganese to a powdered titanium dioxide:

To a solution of 82.8 g of manganese(II) acetylacetonate (0.33 mol) in 750 mL of ethanol, at room temperature, 274.5 g of titanium dioxide powder (Norton) were added at room temperature. An adjustment to alkalinity was then carried out with diluted sodium phenolate solution. The resulting suspension was removed by suction and washed. The manganese doped support was prepared in a slurry with 1500 mL of water and reacted with 600 mL of an aqueous solution containing 50 g of sodium tetrachloropallidate(II) solution with 15% Pd. An adjustment to alkalinity was then carried out with a diluted sodium phenolate solution. The suspension so obtained was removed by suction, washed, and dried at 100EC. The contact catalyst contained 2.5 wt% of Pd and 6 wt% of Mn, each calculated as metal.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 8.6% of diphenylcarbonate; after 2 h, 15.2% of diphenylcarbonate; and after 3 h, 8.2% of diphenylcarbonate were contained in the reaction mixture. 15.0 g of a phenol/water mixture were condensed in the cold trap.

Example 6

a) Application of palladium, copper and molybdenum onto a titanium dioxide extrudate:

200 mL of titanium dioxide extrudate were presoaked with 100 mL of 25% aqueous ammonia solution. Then the support was reacted with a solution consisting of 300 mL of 25% aqueous ammonia solution, 1.44 g of palladium(II) chloride (0.008 mol), 2.76 g of copper(II)-chloride-2-hydrate (0.016 mol) and 3.04 g of ammonium molybdate(VI)-4-hydrate (0.0025 mol). The mixture was rolled for 1 h at 80EC, and the volatile components were then removed at 80EC in a vacuum. After drying under nitrogen at 200EC, a catalyst was obtained with 4.3 g of Pd, 5.2 g of Cu and 8.3 g of Mo per liter of contact catalyst mass.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 3. The analyses showed that: after 1 h, 2.2% of diphenylcarbonate; after 2 h, 4.5% of diphenylcarbonate; and after 3 h, 6.3% of diphenylcarbonate were contained in the reaction mixture. 5.7 g of a phenol/water mixture were condensed in the cold trap.

Example 7

a) Application of palladium and vanadium to a powdered lanthanum oxide

To an HNO_3 acidic solution consisting of 13.8 g of ammonium vanadate (0.12 mol) in 1380 mL of H_2O, at 70EC, 189 g of lanthanum(III) oxide powder (Bayer) were added. The suspension was then removed by suction, dried, and equilibrated for 4 h at 400EC. The vanadium doped support was added, at room temperature, to a solution of 12.5 g of palladium(III) bromide (0.05 mol) and 19 g of sodium bromide (0.18 mol) in 1000 mL of H_2O. The suspension was stirred, removed by suction, washed and dried at 60EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 2.0% of diphenylcarbonate; after 2 h, 3.6% of diphenylcarbonate; and after 3 h, 4.7% of diphenylcarbonate were contained in the reaction mixture. 3.5 g of a phenol/water mixture were condensed in the cold trap.

Example 8

a) Application of palladium and manganese to a powdered iron oxide

To a slurry of 189 g of iron(III) oxide (Bayer) in 1000 mL of H_2O, at room temperature, 200 mL of a solution of 21.6 g of manganese(II)-chloride-4-hydrate (0.11 mol) in H_2O were added. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension was reacted with 300 mL of a solution of 12.5 g of palladium(II) bromide (0.05 mol) and 19 g of sodium bromide (0.18 mol) in H_2O. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension was removed by suction, washed, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 2.9% of diphenylcarbonate; after 2 h, 5.1% of diphenylcarbonate; and after 3 h, 6.7% of diphenylcarbonate were contained in the reaction mixture. 5.1 g of a phenol/water mixture were condensed in the cold trap.

Example 9

a) Application of palladium and manganese to a powdered magnesium oxide

To a slurry of 189 g of magnesium(II) oxide (Bayer) in 1000 mL of H_2O, at room temperature, 200 mL of a solution of 21.6 g of manganese(II) chloride-4-hydrate (0.11 mol) in H_2O and 300 mL of a solution of 12.5 g of palladium(II) bromide (0.05 mol) and 19 g of sodium bromide (0.18 mol) in H_2O were added. The suspension was stirred, washed, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 1.5% of diphenylcarbonate; after 2 h, 2.6% of diphenylcarbonate; and after 3 h, 3.3% of diphenylcarbonate were contained in the reaction mixture. 2.5 g of a phenol/water mixture were condensed in the cold trap.

Example 10

a) Application of palladium and manganese to a powdered activated carbon

To a slurry of 189 g of activated carbon (Norite) in 1000 mL of H_2O, at room temperature, 200 mL of a solution of 21.6 g of manganese(II) chloride-4-hydrate (0.11 mol) in H_2O and 300 mL of a solution of 12.5 g of palladium(II) bromide (0.05 mol) and 19 g of sodium bromide (0.18 mol) in H_2O were added. The suspension was stirred, removed by suction, washed, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate:

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 5.2% of diphenylcarbonate; after 2 h, 9.2% of diphenylcarbonate; and after 3 h, 11.9% of diphenylcarbonate were contained in the reaction mixture. 9.0 g of a phenol/water mixture were condensed in the cold trap.

Example 11

a) Application of palladium and manganese to a powdered silicon dioxide

To a solution of 27.7 g of manganese(II) acetylacetonate (0.11 mol) and 33.3 g of sodium tetrachloropalladate(II) solution with 15% of Pd in ethanol, 189 g of silicon dioxide

(Tolsa) were added. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension was stirred, removed by suction, washed, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 8.1% of diphenylcarbonate; after 2 h, 14.3% of diphenylcarbonate; and after 3 h, 18.6% of diphenylcarbonate were contained in the reaction mixture. 14.1 g of a phenol/water mixture were condensed in the cold trap.

Example 12

a) Application of palladium and manganese to a powdered aluminum oxide

To a solution of 27.7 g of manganese(II) acetylacetonate (0.11 mol) and 33.3 g of sodium tetrachloropalladate(II) solution with 15% of Pd in ethanol, 189 g of aluminum(III) oxide (Rhone Poulenc) were added. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension was stirred, removed by suction, washed, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 5.8% of diphenylcarbonate; after 2 h, 10.2% of diphenylcarbonate; and after 3 h, 13.2% of diphenylcarbonate were contained in the reaction mixture. 10.0 g of a phenol/water mixture were condensed in the cold trap.

Example 13

a) Application of palladium and manganese to a powdered manganese oxide

To a solution of 27.7 g of manganese(II) acetylacetonate (0.11 mol) and 10.4 g of palladium(II) acetate (0.05 mol) in ethanol, 189 g of manganese(IV) oxide (Fluka) were added. The suspension was reduced in the rotation evaporator.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 3.7% of diphenylcarbonate; after 2 h, 6.6% of diphenylcarbonate; and after 3 h, 8.6% of diphenylcarbonate were contained in the reaction mixture. 6.5 g of a phenol/water mixture were condensed in the cold trap.

Example 14

a) Application of palladium and cobalt to a powdered manganese oxide

To a solution of 12.5 g of palladium(II) bromide (0.05 mol), 24.2 g of cobalt(II) chloride 6-hydrate (0.1 mol) and 19 g of sodium chloride (0.18 mol) in H_2O, 189 g of manganese(IV) oxide (Fluka) were added. The suspension was stirred, the alkalinity adjusted with soda lye, removed by suction, washed, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 3.5% of diphenylcarbonate; after 2 h, 6.1% of diphenylcarbonate; and after 3 h, 8.0% of diphenylcarbonate were contained in the reaction mixture. 6.1 g of a phenol/water mixture were condensed in the cold trap.

Example 15

a) Application of palladium and manganese to activated carbon extrudates

200 mL of activated carbon extrudes (Norit) were soaked with 58 mL of soaking fluid, containing 21.6 g of manganese(II) chloride 4-hydrate (0.11 mol) and 33.3 g of sodium tetrachloropalladate(II) solution with 15% of Pd in H_2O. Then a drying step under nitrogen was carried out.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1, except that the catalyst was fixed in a mesh wire basket. The analyses showed that: after 1 h, 3.2% of diphenylcarbonate; after 2 h, 5.6% of diphenylcarbonate; and after 3 h, 7.3% of diphenylcarbonate were contained in the reaction mixture. 5.5 g of a phenol/water mixture were condensed in the cold trap.

Example 16

a) Application of palladium and manganese to a powdered montmorillonite

To a solution of 27.7 g of manganese(II) acetylacetonate (0.11 mol) in ethanol, 189 g of montmorillonite (Fluka) were added. An adjustment to alkalinity was then carried out with diluted soda lye. The suspension was removed by suction and washed. The manganese-doped support was prepared in a slurry with 1000 mL of H_2O and with 33.3 g of sodium

tetrachloropalladate(II) solution with 15% of Pd. The suspension was removed by suction, and dried at 100EC.

b) Use of the supported catalyst for the manufacture of diphenylcarbonate

The use of the supported catalyst for the manufacture of diphenylcarbonate was carried out as in Example 1. The analyses showed that: after 1 h, 3.4% of diphenylcarbonate; after 2 h, 6.0% of diphenylcarbonate; and after 3 h, 7.8% of diphenylcarbonate were contained in the reaction mixture. 5.9 g of a phenol/water mixture were condensed in the cold trap.

Claims

1. Supported catalysts, containing in the reactive state (i) a platinum metal, platinum metal halide or a platinum metal halide-containing complex compound or a compound which can be transferred under the conditions of the reaction into a platinum metal, platinum metal halide or a platinum metal halide-containing complex compound, in a quantity of 0.01-15 wt%, preferably 0.05-10 wt%, calculated as platinum metal and with respect to the total weight of the catalyst, and (ii) a cocatalytically acting metal compound from the groups IB, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, the iron group (atomic numbers 26-28) or the rare earth metals (atomic numbers 58-71) of the periodic table of elements (Mendelyeer) in a quantity of 0.01-15 wt%, preferably 0.05-10 wt%, calculated as metal, and with respect to the total weight of the catalyst.

2. Catalyst according to Claim 1, characterized in that as platinum metal Pd or Rh, preferably Pd, and as metal, metal halide or metal halide-containing complex compound is used.

3. Catalyst according to Claim 1, characterized in that, as cocatalytic metal compound, a compound of a metal from the group comprising Mn, Cu, Co, V, Zn, Ce and Mo is used, preferably from the group comprising Mn, Cu, Co, Ce and Mo.

4. Method for the manufacture of an aromatic compound having the formula

R-O-CO-O-R

in which

R denotes substituted or unsubstituted C_6-C_{12} aryl, preferably substituted or unsubstituted phenyl, and, in particular, unsubstituted phenyl,

by reacting an aromatic hydroxy compound having the formula

R-O-H

in which R has the above indicated meaning,
with carbon monoxide and oxygen in the presence of quaternary ammonium or phosphonium salt and a base at 30-200EC, preferably 30-150EC, in particular 40-120EC, and at a pressure of 1-150 bar, preferably 2-50 bar, and in particular 5-25 bar, characterized in that a supported catalyst according to Claim 1 is used.

5. Catalyst according to Claim 1, which can be manufactured by the simultaneous or subsequent application of a platinum metal compound and a cocatalytically acting compound on a support, where, as platinum metal compound, a platinum metal halide or a platinum metal halide complex compound is used, or a compound is used which can be converted under the reaction conditions into a platinum metal, platinum metal halide, or a platinum metal halide-containing complex compound; or the platinum metal halide or the platinum metal halide complex compound is formed, on the catalyst support from a halide-free platinum metal compound and a halide-containing compound; or from a halide-free platinum metal compound by the reaction with a reduction agent at 0-500EC, first to form the elemental platinum metal, and followed by the reaction of the latter with gaseous hydrogen halide or gaseous halogen at 20-600EC on the catalyst support.

6. Catalyst according to Claim 5, characterized in that platinum metal halides or complexes containing platinum metal halides are prepared, where the complexes contain nitriles, CO, olefins, amines, phosphines, water or another halide, or are prepared by the simultaneous or subsequent application of a platinum metal compound from the group of the acetates, nitrates, acetylacetonates, oxalates and hydroxides, and a halogen-containing compound from the group comprising NaCl, NaBr, $MgCl_2$, $MgBr_2$, $MnCl_2$, $MnBr_2$, $CuCl_2$, and tetrabutylammonium bromide on the support.

7. Catalyst according to Claim 5, characterized in that, for the application of the cocatalytically acting compound, a halide, oxide, carboxylate of C_2-C_6 carboxylic acids, diketonate, nitrate or a complex compound of a cocatalytically acting metal is used which compound can contain CO, olefins, amines, nitriles, phosphines or a halide.

8. Method according to Claim 4, characterized in that the supported catalyst is used in a continuous mode in countercurrent or cocurrent mode or with fixed catalysts in the stirred vessel, bubble column reactor or in the trickling phase at the solid bed catalyst with a load of 0.01-20 g of aromatic hydroxy compound per gram of supported catalyst per hour, preferably 0.05-10 g of aromatic hydroxy compound per gram of supported catalyst per hour, and in particular 0.1-5 g of aromatic hydroxy compound per gram of supported catalyst per hour, and, in the case of operating using a suspension in stirred vessel or bubble columns, in quantities of 0.001-50 wt%, preferably 0.01-20 wt%, and in particular 0.1-10 wt%, with respect to the used quantity of aromatic hydroxy compound.

9. Method according to Claim 4, characterized in that one uses, as base, a tertiary amine, alkali phenolate or alkali salt of weak acids, particularly alkali carboxylates and/or -phenolates, and in particular sodium phenolate.

10. Method according to Claim 4, characterized in that one uses as quaternary salt tetraalkylammonium- or -phosphonium salts, preferably tetraalkylammonium salts, and in particular tetrabutylammonium bromide.

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PLATINUM METAL-CONTAINING SUPPORTED CATALYSTS AND METHOD FOR THE PREPARATION OF DIARYLCARBONATES

Inventors:	Dr. Hans-Josef Buysch 47809 Krefeld (DE)
	Dr. Carsten Hesse 47800 Krefeld (DE)
	Dr. Jörg-Dietrich Jentsch 45468 Mühlheim (DE)
	Dr. Johann Rechner 47906 Kempen (DE)
	Dr. Eberhard Zirngiebl 51061 Cologne (DE)
Applicant:	BAYER AG 51368 Leverkusen (DE)

In the method for the preparation of an aromatic carbonate from an aromatic hydroxy compound, CO and O_2 in the presence of quaternary salts and a base using a platinum metal catalyst and a cocatalyst, it is advantageous to use supported catalysts, which contain, in the reactive state (i) a platinum metal, a platinum metal halide, or a platinum metal halide complex compound, and (ii) a cocatalytically acting metal compound from the groups IB, IIB, IIIA, IIIB, IVA, IVB, VB, VIB, VIIB, the iron group (atomic numbers 26-28) or the rare earth metals (atomic numbers 58-71) of the periodic table of elements (Mendelyeer), always in a quantity of 0.01-15 wt%, calculated as metal and with respect to the total weight of the catalyst.

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EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int Cl.^{6x})
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	
X,D	EP-A-0 614 876 (MITSUBISHI PETROCHEMICAL CO., LTD.) IN PARTICULAR PAGE 4, LINES 3-7 AND PAGE 5, LINE 32 ---	1-4	B01J23/56 C07C68/00 C07C69/96
X	EP-A-0 607 943 (DAICEL CHEMICAL INDUSTRIES CO., LTD.) IN PARTICULAR PAGE 13, EXAMPLE 7, AND CLAIMS 7-14 ---	1-3	
X	EP-A-0 581 240 (UBE INDUSTRIES, LTD.) * entire document * ---	1-3	TECHNICAL FIELDS SEARCHED (Int. Cl.^{6})
X	EP-A-0 464 460 (BAYER AG) * entire document * ---	1-3	C07C
A,P	EP-A-0 654 461 (BAYER AG) * entire document * ----	4	

The present search report has been drawn up for all claims.

Place of search	Date of completion of the search	Examiner
THE HAGUE	January 21, 1997	Devisme, F

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.
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A: Technological background.
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